

09/05/00

PTO/SB/05 (4/98)

Approved for use through 09/30/2000. OMB 0651-0032

Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Please type a plus sign (+) inside this box → ☒

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

**UTILITY**  
**PATENT APPLICATION**  
**TRANSMITTAL**

Attorney Docket No. JSS-0005  
 First Inventor or Application Identifier Alla Jurieva Krylova  
 Title Fischer-Tropsch Catalyst Enhancement  
 Express Mail Label No. EL02816181US

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

**APPLICATION ELEMENTS**

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents  
 Box Patent Application  
 Washington, DC 20231

1. ☒ \* Fee Transmittal Form (e.g., PTO/SB/17) (Submit an original and a duplicate for fee processing)2. ☒ Specification (preferred arrangement set forth below)Total Pages **22**

- Descriptive title of the invention
- Cross References to Related Applications
- Statement Regarding Fed sponsored R & D
- Reference to Microfiche Appendix
- Background of the Invention
- Brief Summary of the Invention
- Brief Description of the Drawings (if filed)
- Detailed Description
- Claim(s)
- Abstract of the Disclosure

3. ☐ Drawing(s) (35 U.S.C. 113)Total Sheets 4. ☒ Oath or DeclarationTotal Pages **2**a. ☒ Newly executed (original or copy)b. ☐ Copy from a prior application (37 C.F.R. § 1.53(b)) (for continuation/divisional with Box 16 completed)i. ☐ **DELETION OF INVENTOR(S)**

Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

☐ Microfiche Computer Program (Appendix)6. ☐ Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)a. ☐ Computer Readable Copyb. ☐ Paper Copy (identical to computer copy)c. ☐ Statement verifying identity of above copies**ACCOMPANYING APPLICATION PARTS**7. ☐ Assignment Papers (cover sheet & document(s))8. ☐ 37 C.F.R. § 3.73(b) Statement (when there is an assignee)☐ Power of Attorney9. ☐ English Translation Document (if applicable)10. ☐ Information Disclosure Statement (IDS)/PTO-1449☐ Copies of IDS Citations11. ☐ Preliminary Amendment12. ☒ Return Receipt Postcard (MPEP 503) (Should be specifically itemized)13. ☐ \* Small Entity Statement(s) (PTO/SB/09-12)☐ Statement filed in prior application,  
Status still proper and desired14. ☐ Certified Copy of Priority Document(s) (if foreign priority is claimed)15. ☐ Priority of application Serial No. \_\_\_\_\_ Filed on \_\_\_\_\_ in \_\_\_\_\_  
(Country) is claimed under 35 U.S.C. 11916. ☐ Other: \_\_\_\_\_

\* NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED  
 (37 C.F.R. § 1.27, EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

## 16. FEE CALCULATION

CLAIMS AS FILED				
(1) For	(2) Number Filed	(3) Number Extra	(4) Rate	(5) Basic Fee \$690.00
Total Claims	19 - 20	0	x 18.00	0
Independent Claims	1 - 3	0	x 78.00	0
Multiple Dependent Claim Fee			+ 260.00	0
TOTAL FILING FEE				\$690.00

☐ Fee for recording Assignment (\$40.00).

☒ Please charge Deposit Account No. 05-1330 in the amount of \$ 690.00.

☒ The Commissioner is hereby authorized to charge any additional fees under 37 CFR 1.16 and 1.17 which may be required during the entire pendency of the application, or credit any overpayment, to Deposit Account No. 05-1330. A duplicate copy of this Form is enclosed.

17. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.: \_\_\_\_\_ / \_\_\_\_\_

Prior application information: Examiner: \_\_\_\_\_ Group / Art Unit: \_\_\_\_\_

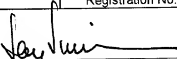
For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

## 18. CORRESPONDENCE ADDRESS

☐ Customer Number or Bar Code Label ☒ Correspondence address below

(Insert Customer No. or Attach bar code label here)

Name	Jay Simon				
	ExxonMobil Research and Engineering Company (formerly Exxon Research and Engineering Company)				
Address	P. O. Box 900				
City	Annandale	State	New Jersey	Zip Code	08801-0900
Country	United States of America	Telephone	(908) 730-3673	Fax	(908) 730-3649

Name (Print / Type)	Jay Simon	Registration No. (Attorney / Agent)	23,067
Signature		Date	8/31/00

☒ "Express Mail" mailing label number EL028161816US Date of Deposit September 1, 2000

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

PHYLLIS A. TAYLOR

(Typed or printed name of person mailing paper or fee)

(Signature of person mailing paper or fee)

APPLICATION FOR UNITED STATES PATENT

FISCHER-TROPSCH CATALYST ENHANCEMENT (JSS-0005)

Applicants: Alla Jurieвна Krylova  
Albert L'vovich Lapidus  
Lilia Vadimovna Sineva  
Michel A. Daage  
Russell John Koveal

"EXPRESS MAIL" mailing label

number EL028161816US

Date of Deposit September 1, 2000

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

PHYLLIS A. TAYLOR

(Typed or printed name of person mailing paper or fee)

Phyllis A. Taylor

(Signature of person mailing paper or fee)

## FISCHER-TROPSCH CATALYST ENHANCEMENT (JSS-0005)

This invention relates to a process for the activation of dispersed active metal catalysts that enhances their activity and selectivity in the production of higher hydrocarbons from synthesis gas.

### Background of the Invention

The production of higher hydrocarbon materials from synthesis gas, i.e. carbon monoxide and hydrogen, commonly known as the Fischer-Tropsch ("F-T") process, has been in commercial use for many years. Such processes rely on specialized catalysts. The original catalysts for the Fischer-Tropsch synthesis were nickel. Nickel is still the preferred catalyst for hydrogenation of fats and specialty chemicals. Over the years, other metals, particularly iron and cobalt, have been preferred in the Fischer-Tropsch synthesis of higher hydrocarbons whereas copper has been the catalyst of choice for alcohol synthesis. Cobalt is particularly preferred for Fischer-Tropsch synthesis due its high productivity and comparatively low methane selectivity. As the technology of these syntheses developed over the years, the catalysts became more refined and were augmented by other metals and/or metal oxides that function to promote their catalytic activity. These promoter metals include the Group VIII metals, such as platinum, palladium, rhenium, ruthenium and iridium. Metal oxide promoters include the oxides of a broader range of metals, such as molybdenum, tungsten, zirconium, magnesium, manganese and titanium. Those of ordinary skill in the art will appreciate that the choice of a particular metal or alloy for fabricating a catalyst to be utilized in Fischer-Tropsch synthesis will depend in large measure on the desired product or products.

Particularly suited for the production of hydrocarbons by Fischer-Tropsch synthesis from synthesis gas are Dispersed Active Metals ("DAM") which are primarily, i.e. at least about 50 wt. %, preferably at least 80 Wt. %, composed of one or a mixture of metals such as described above and are, without further treatment, capable of catalyzing Fischer-Tropsch synthesis. DAM catalysts may be prepared by any of a number of art-recognized processes.

In 1924, M. Raney prepared a nickel hydrogenation catalyst by a process known today as the Raney Process. For purposes of simplicity, the term "Raney" will be utilized herein as a generic term to describe the process, alloys and catalysts obtained thereby. This specific synthesis, in essence, comprises forming at least a binary alloy of metals, at least one of which can be extracted, and extracting it thereby leaving a porous residue of the non-soluble metal or metals that possesses catalytic activity. The residue, or non-extractable, catalyst metals are well known to those skilled in the art and include Ni, Co, Cu, Fe and the Group VIII noble metals. Likewise, the leachable or soluble metal group is well known and includes aluminum, zinc, titanium and silicon, typically aluminum. Once alloys are formed of at least one member of each of these groups of metals, they are ground to a fine powder and treated with strong caustic, such as sodium hydroxide, to leach the soluble metal.

There exist many variations of the basic preparation of Raney catalysts such as, for example, deposition of alloys onto a performed support by flame spraying, (U.S. Patent No. 4,089,812), formation of the alloy by surface diffusion of aluminum on a non-leachable metal substrate (U.S. Patent No. 2,583,619), and forming pellets from the powdered alloys for use in fixed bed reactions vessels (U.S. Patent No. 4,826,799, U.S. Patent No. 4,895,994 and U.S. Patent No. 5,536,694). These developments have made possible the use of shaped Raney catalysts in fixed bed reaction vessels.

A preferred reactor carrying out for Fischer-Tropsch reactions utilizing DAM catalysts is the slurry bubble column developed by Exxon Research & Engineering Company. This reactor, which is ideally suited for carrying out highly exothermic, three-phase catalytic reactions, is described in U.S. Patent No. 5,348,982. In such reactors, the solid phase catalyst is dispersed or held in suspension in a liquid phase by a gas phase that continuously bubbles through the liquid phase. The catalyst loading in slurry bubble reactors can vary within a broad range of concentrations, but must remain short of the so-termed "mud limit" where the concentration becomes so high that mixing and pumping of the slurry become so difficult that practical operation is no longer possible. The use of high metal-loading catalysts or bulk metal catalysts is preferred in slurry bubble reactors in order to maximize the productivity of both catalyst and reactor.

An extensive review of process of forming DAM catalysts can be found in "Active Metals", Edited by Alois Furstner, published by VCH Verlagsgesellschaft mbH, D-69451 Weinheim (FRG) in 1996 and the references cited therein. Methodologies described therein include the Reike method, the use of ultrasound, reduction of metal salts, colloids, nanoscale cluster and powders. Other relevant references include, for example, the preparation of amorphous iron catalyst by high intensity sonolysis of iron pentacarbonyl, Suslick et al., Nature, Vol. 353, pp 414-416 (1991) and the formation of single domain cobalt clusters by reduction of a cobalt salt with hydrazine, Gibson et al., Science, Vol. 267, pp 1338-1340, (1998). Finally, intermetallic alloys, particularly those known for forming metal hydrides, such as  $\text{LaCo}_5$ , can be formed into a fine powder by the application of hydrogen adsorption/desorption cycles. DAM catalysts can also be prepared by thermal or chemical decomposition of metal formates or oxalates. These methods are given as

examples and are not intended in any way to limit the term "DAM" as utilized in the context of the present invention.

One of the primary characteristics of DAM catalysts is that, in their dry form, they are generally pyrophoric. For this reason, they are generally stored and shipped in airtight containers, typically as a slurry in an appropriate solvent, such as water or oil, or coated with a removable protective layer of an air-impervious material, such as wax. We are not aware of any DAM catalysts that are not used as they are formed, i.e. without any further treatment following extraction of the leachable metal and subsequent drying steps as described above. On the opposite end of the cycle, the manufacturers of DAMs recommend that spent catalysts, i.e. those no longer economically effective, must undergo deactivation in order that they may be safely disposed of. Such deactivation is generally achieved via oxidation of the metal by air oxidation or treatment with dilute bleach solution.

It will be appreciated that a means of enhancing the activity of the catalyst would greatly increase its value in the process. Another important aspect of the value of a catalyst is its selectivity which is the ratio of the percent of feed material converted to desired higher hydrocarbons to that of short chain hydrocarbons produced, primarily methane, commonly referred to as "methane selectivity". In copending patent application Docket No. 33737 there is disclosed and claimed a process called slurry low temperature oxidation whereby the activity and methane selectivity of a DAM catalyst are significantly enhance. In accordance with the present invention, it has been found that a modification of the slurry low temperature oxidation further enhances the activity and methane selectivity of DAM catalysts.

### Summary of the Invention

In accordance with the present invention, Dispersed Active Metal ("DAM") Fischer-Tropsch catalysts are enhanced both in activity and methane selectivity by low temperature oxidative deactivation in a slurry phase to form an oxidized catalyst precursor comprising said metals and at least one of hydroxides thereof and oxides, which differs compositionally from that obtained by conventional high temperature oxidation utilizing an oxygen-containing gas. The activity and methane selectivity of the DAM catalyst is further enhanced by the addition to the DAM catalyst prior to, during or subsequent to the oxidation of one or more reducible salts of a group of metal promoters, followed by reductive reactivation of the oxidized catalyst precursor with a hydrogen-containing gas at elevated temperature thereby also reducing the salts of the metal to the metallic state and depositing it on the surface of the catalyst particles.

### Detailed Description of the Invention

It is well known to those skilled in the art of Fischer-Tropsch synthesis chemistry that Group VIII metal surfaces exhibit higher activities for catalytic reactions such as hydrogenation, methanation and Fischer-Tropsch synthesis when subjected to a high temperature oxidation-reduction (O-R) cycle. Such "activation" techniques are reviewed in Applied Catalysis, A. General 175, pp 113-120 (1998) and citations therein. A series of patents, e.g. U.S. Patent Nos. 4,492,774; 4,399,234; 4,585,789 and 4,670,414 disclose activation of a cobalt catalyst by a reduction/oxidation/reduction (R-O-R) cycle. So far as we are aware, all such oxidation/reduction and reduction/oxidation/reduction cycles described in the literature are effected by treating a solid catalyst with an oxygen-containing gas at high temperatures. This treatment results in the



formation of the most stable oxide of the metal, i.e. in the instance of cobalt,  $\text{Co}_3\text{O}_4$ . All DAMs treated in accordance with the invention are characterized by the capacity to form more than one oxide. Heretofore, those practicing the process described above have sought to completely oxidize such DAMs to the highest oxidation state oxide, which corresponds to the most stable oxide.

In the activation treatments described above, the oxygen content of the treating gas in the oxidation step varies from as low as 15 ppm to pure oxygen and the temperatures typically are between about 200°C to 600°C. Several publications dealing with these activation methodologies also stress the importance of controlling the exothermicity of the reaction to avoid sintering of the cobalt oxide particles since that may be detrimental to the activity of the final catalyst. We have found that this latter observation is even more critical with regard to the oxidation of DAM catalysts because of their high metal content, particularly those that may also contain active hydrogen species as in Raney catalysts or metal hydrides.

Significant enhancement in both the activity and methane selectivity for Fischer-Tropsch synthesis is realized by treating a DAM catalyst with an oxidation/reduction cycle wherein the oxidation is carried out in a slurry phase at low temperature. By low temperature is meant a temperature below 200°C, preferably below 100°C. The oxidation is effected by bubbling a gaseous oxidant through a slurry of the DAM catalyst, or by the slurry itself formed from or combined with an aqueous solution of a suitable oxidant. Typical conditions for the oxidative deactivation of a DAM catalyst utilizing an oxidative gas are as follows: ratio of liquid to DAM by volume - at least about 3:1, preferably at least about 5:1; temperature - from about 25°C to 100°C, preferably from about 50°C to 80°C; total pressure - from about 15 to 300 psia, preferably from about 15 to

100 psia; contact time for the DAM in the slurry - at least one hour, preferably until the DAM has lost pyrophoricity; and gas flow rate - at least 100 cc/min. Typical oxidative gases in addition to oxygen include ozone and nitrogen oxides, i.e. nitrous oxide and nitric oxide all of which may be utilized in pure form, but typically are mixed with one or more inert diluent gases. Wherein oxygen is utilized, for example, typically air is caused to flow into the slurry. Alternatively, pure oxygen can be mixed with an inert gas in from about 1 to 50%, preferably from about 5 to 25% by volume.

Wherein the oxidative treatment is carried out utilizing a dilute solution of an oxidant, the oxidant is chosen so as not to introduce substances into the slurry that are recognized as being permanent poisons of the Fischer-Tropsch synthesis, e.g. ionic forms of chlorine, bromine, phosphorus and sulfur. Included within the scope of oxidants in solution are solutions of compounds that form oxidants in situ upon contact with air, for example, certain alcohols will form hydroperoxides upon contact with air. Preferred oxidants include nitric acid and inorganic nitrates, for example, ammonium nitrate, hydrogen peroxide, and art-recognized organic peroxides or hydroperoxides. Those skilled in the art will appreciate that the concentration of individual oxidants will vary according to their oxidizing capacity. In general, the amount of the oxidant in the slurry and the duration of the oxidation are sufficient to insure oxidation to a point such that the resulting dry DAM material would not exhibit uncontrollable pyrophoric responses upon exposure to ambient air and moisture but not so great as to cause unwanted secondary reactions, such as dissolution or extraction of the active metal ions in the catalyst.

The liquid utilized to form the slurry is preferably water, however, organic solvents may be utilized provided that they do not introduce any known poison of the Fischer-Tropsch synthesis and are non-reactive at the conditions of

the oxidation treatment. Hydrocarbons, particularly those derived from the Fischer-Tropsch synthesis itself are appropriate and may be used with either an oxygen-containing gas or dilute solution of the oxidants named above that are soluble therein, such as the organic peroxides. Further, mixtures of water and organic solvents miscible therewith can be utilized as well. Mixtures of water with immiscible solvents can also be utilized in combination with suitable dispersing or emulsifying agents present to form a continuous phase, i.e. an emulsion. Other suitable liquids include dense fluids, for example, supercritical fluids such as liquid phase light, i.e. C3-5 alkanes, cyclopentane and the like. Preferred mixed liquids include, without any intended limitation, water/ lower alkanols, water/Fischer-Tropsch products, and water/alkanols/alkanes. Solutions of the one or more reducible salts of the promoter metals may be utilized in whole or in part to form the slurry as will be described below.

The oxidative treatment described herein may be carried out in any reactor apparatus suitable for slurry reactions including, with no limitation intended, fixed bed reactors, moving bed reactors, fluidized bed reactors, slurry reactors, bubbling bed reactors and the like. Irrespective of whether the slurry reactor is operated as a dispersed or slumped bed, the mixing conditions in the slurry will typically be somewhere between the theoretical limiting conditions of plug flow and complete back mixing.

The product of the low temperature oxidation treatment of a DAM catalyst as described above is a mixture of metallic and oxidic species. This is the result of the fact that the metals in the DAMs can exist in more than one oxidation state and, in the subject treatment, a significant portion of the active metal of the DAM is oxidized to a lower oxidation state. In contrast, the prior art high temperature oxidation treatments result in complete oxidation of the active metal to the highest, and most stable, oxidation state. For example, in the

subject treatment, a significant portion of cobalt metal is oxidized to  $\text{CoO}$  and/or  $\text{Co(OH)}_2$  rather than  $\text{Co}_3\text{O}_4$ , iron metal is oxidized to  $\text{FeO}$  and/or  $\text{Fe(OH)}_2$  rather than  $\text{Fe}_3\text{O}_4$ . Additionally, when the slurry in which the treatment is effected contains water, hydroxides of the metals will be formed as part of the mixture referred to above. This mixture is in fact an oxidized catalyst precursor wherein, on a mole percent basis, not more than 50% of the active metal present is in the form of the oxide of the highest oxidation state, and the highest oxidation state of the metal in combination with the amount in the metallic state does not exceed 85% of the active metal present, the remainder being lower oxidation state oxides and/or hydroxides. Preferably, not more than 25% of the active metal present is in the form of the oxide of the highest oxidation state, and the highest oxidation state of the metal in combination with the amount in the metallic state does not exceed 60% of the active metal present, the remainder being lower oxidation state oxides and/or hydroxides.

The oxidative treatment is regarded as complete the DAM no longer exhibits uncontrollable pyrophoricity, the resulting oxidized catalyst precursor is recovered from the slurry and dried. By not exhibiting uncontrollable pyrophoricity is meant that, upon filtering the DAM in air, the temperature should not rise above  $200^\circ\text{C}$ . The oxidized precursor may be rinsed to remove any remaining solution and then combined with the solution of one or more reducible salts of promoters metals, or may be recovered by physical separation and dried before being combined with the solution of the reducible salts as described below.

We have found that the activity of a DAM catalyst, already enhanced by slurry low temperature oxidation as described above, can be further improved by the addition thereto of small amounts of certain reducible metals that are recognized by those of ordinary skill in the art as promoters for cobalt. It is

considered unexpected that the metals utilized in the subject process enhance the desirable properties of the DAM catalyst particles because not all members of the group of reducible metals recognized as promoters for cobalt have been found to be beneficial in the process of the invention. In accordance with the present invention, one or more members selected from the group consisting of rhenium, ruthenium, palladium, iron and cobalt added to the enhanced DAM catalyst as described herein has been found to further improve at least one of its performance characteristics. Cobalt is included in the list even though the DAM itself may be at least partially cobalt since the present process is intended to enhance the properties and activities of DAMs and the addition of metallic cobalt itself by the process of the invention is beneficial in comparison to the DAM only enhanced by slurry low temperature oxidation as described above. Also, other reducible metals, such as copper, may be added by the present process and may be beneficial for other applications, e.g. converting syngas to oxygenates.

In accordance with the present invention, one or more suitable salts of the reducible metals of the invention is added to the DAM in an amount sufficient to provide a total metal addition of from about 0.01 to about 20, preferably from about 0.1 to about 10 percent by weight, based on the catalyst metal in the DAM. Suitable salts utilized to provide the reducible metals to the DAM are those that will solubilize the metal in a solvent that can conveniently be utilized for the addition, are compatible with the DAM and do not introduce appreciable quantities of potential contaminants into the DAM. Although other solvents may be utilized, water is preferred for the addition of the reducible metals of the invention. It is within the scope of the present invention to utilize a salt, such as a chloride, that would ordinarily be considered as a source of contamination because the treatment of the DAM with hydrogen-containing gas at elevated temperatures reduces the metal salt to the metallic state and forms a compound,

such as hydrogen chloride, that will volatilize at those temperatures and can be easily removed from the reactor. Preferred salts are the chlorides, such as ruthenium trichloride, the nitrates, such as cobalt nitrate, an organic salt such as cobalt acetate, a compound salt such as ammonium perchlorate and the like.

One or more reducible salt of the promoter metals of the present invention may be added to the DAM as a solution in a suitable solvent prior to, during or subsequent to completion of the oxidation, but prior to reduction with hydrogen at elevated temperature. It is preferred to recover the oxidized catalyst precursor and rinse any remaining solution containing oxidant from it prior to the addition of the solution of metal salt as disclosed herein. The oxidized catalyst precursor may be dried and stored if it is desired to carry out the addition of the subject reducible metals in a separate operation. In either event, a solution of the salt of the reducible metals of the invention is combined and thoroughly mixed for a time sufficient to assure uniform distribution of the salt. The mixture of the oxidized catalyst precursor and one or more salts is then recovered from the physical separation, such as filtrating or centrifugation/decanting, and dried. The mixture may be dried under vacuum or under an inert atmosphere at a temperature of from about 50° to 150°C. Preferably, the mixture is dried under air flow at a temperature above 100°C for at least one hour. In another preferred embodiment, the initial drying of the oxidized catalyst precursor is carried out in air as described and the second drying after one or more salts of the subject reducible metals have been added carried out under an inert atmosphere.

The mixture of one or more salts of the reducible promoter metals of the invention and the oxidized catalyst precursor is then converted to the active catalyst and promoter metal, respectively, by reduction with hydrogen-containing gas at temperatures of from about 200°C to 600°C, preferably from about 300°C to 450°C, most preferably from about 340°C to 400°C. Hydrogen

partial pressure during the reduction would range from about 1 to 100 atmospheres, preferably from about 1 to 40 atmospheres. Typical Fischer-Tropsch activities of DAM catalysts activated in accordance with the process of the present invention are at least 120%, more frequently at least 150% of that of the original DAM. By the same token, methane selectivity of the DAMs are reduced by the present process to below 80%, more frequently below 60% of the original DAM. As those of ordinary skill in the art are aware, methane selectivity is enhanced when the percentage is reduced, hence a reduction in methane selectivity is a significant improvement.

The catalysts formed from DAMs in accordance with the activation process of the invention are used in synthesis processes for the formation of higher hydrocarbons wherein liquid and gaseous products are formed by contacting a syngas comprising a mixture of hydrogen and carbon monoxide with shifting or non-shifting conditions, preferably the latter in which little or no water gas shift takes place. The process is carried out at temperatures of from about 160°C to 260°C, pressures of from about 5 atm to about 100 atm, preferably from 10 to 40 atm, and gas space velocities of from about 300 V/Hr/V to about 20,000 V/Hr/V, preferably from about 1,000 V/Hr/V to about 15,000 V/Hr/V. The stoichiometric ratio of hydrogen to carbon monoxide is about 2.1:1 for the production of higher hydrocarbons. This ratio can vary from about 1:1 to 4:1, preferably from 1.5:1 to 2.5:1, more preferably from 1.8:1 to 2.2:1. These reaction conditions are well known to those skilled in the art and a particular set of reaction conditions can readily be determined from the parameters given herein. The reaction may be carried out in virtually any type of reactor, e.g. fixed bed, moving bed, fluidized bed and the like. The hydrocarbon-containing products formed in the process are essentially sulfur and nitrogen free.

The hydrocarbons produced in a process as described above are typically upgraded to more valuable products by subjecting all or a portion of the C5+ hydrocarbons to fractionation and/or conversion. By "conversion" is meant one or more operations in which the molecular structure of at least a portion of the hydrocarbon is changed and includes both non-catalytic processing, e.g. steam cracking, and catalytic processing, e.g. catalytic cracking, in which the portion, or fraction, is contacted with a suitable catalyst. If hydrogen is present as a reactant, such process steps are typically referred to as hydroconversion and variously as hydroisomerization, hydrocracking, hydrodewaxing, hydrotreating and the like. More rigorous hydrotreating is typically referred to as hydrotreating. These reactions are conducted under conditions well documented in the literature for the hydroconversion of hydrocarbon feeds, including hydrocarbon feeds rich in paraffins. Illustrative, but non-limiting, examples of more valuable products from such feeds by these processes include synthetic crude oil, liquid fuel, emulsions, purified olefins, solvents, monomers or polymers, lubricant oils, medicinal oils, waxy hydrocarbons, various nitrogen- or oxygen-containing products and the like. Examples of liquid fuels includes gasoline, diesel fuel and jet fuel, while lubricating oil includes automotive oil, jet oil, turbine oil and the like. Industrial oils include well drilling fluids, agricultural oils, heat transfer oils and the like.

It is understood that various other embodiments and modifications in the practice of the invention will be apparent to, and can be readily made by, those of ordinary skill in the art without departing from the scope and spirit of the invention as described above. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the exact description set forth above, but rather that the claims be construed as encompassing all of the features of patentable novelty that reside in the present invention, including all the features and embodiments that would be treated as equivalents thereof by those skilled in



the art to which the invention pertains. The invention is further described with reference to the following experimental work.

Example 1: Treatment of Cobalt Catalyst by Slurry Low Temperature Oxidation

A slurry of about 1200 grams of commercial cobalt catalyst (Raney® 2700) in water was placed in a 4 liter beaker and stirred with a Teflon®-coated stirring blade. A total of 1320 cc of 0.5N nitric acid solution was added to the slurry by slow addition. During the addition, the temperature of the slurry rose to about 60°C and a strong ammonia odor developed. The slurry was stirred for an additional hour following completion of the addition. During the oxidation of the catalyst, the pH of the slurry became basic due to the reduction of the nitrate ions to ammonium ions. The total amount of nitrate ions added was adjusted in order to achieve a complete consumption of the hydrogen dissolved in the catalyst and the native hydrogen generated by the acidic oxidation of the metal in the catalyst. Further addition of nitric acid would result in a dissolution of cobalt ions into the solution, evidenced by a pink coloration, which is undesirable. The deactivated catalyst was filtered, washed three times with deionized water recovered by filtration. During the filtration, the solids were again washed three times with deionized water. The solids were dried overnight in a vacuum oven at 60°C. The catalyst was further treated in flowing air at 120°C to complete passivation. The passivated catalyst was stored as is without additional storage precautions, yield 946.6 grams of dried, enhanced, passivated Raney cobalt catalyst.

Example 2: Preparation of Reducible Metal Promoted Raney Cobalt Catalyst

An appropriate quantity of the reducible salt of the metal promoters to be tested to provide the desired amount of the metal on 30.0 grams of passivated Raney cobalt catalyst was dissolved in 12 ml of distilled water. The resulting solution was added to 30.0 grams of the passivated catalyst prepared in Example 1 and stirred for 10 minutes. The material was then dried for 30-45 minutes on a steam bath. After drying, the catalyst was mixed with 30-40 ml of 3-4mm sized quartz particles. The mixture was placed into a reactor. Air was passed through the reactor and it was heated to 400°C and held under flowing air for five hours. The mixture was removed from the reactor and the quartz particles and catalyst were separated by sieving. The metals and their salts utilized were as follows: Rhenium ( $\text{NH}_4\text{ReO}_4$ ), Ruthenium ( $\text{RuCl}_3$ ), Palladium ( $\text{PdCl}_3$ ), and Platinum ( $\text{H}_2\text{PtCl}_6$ ).

Example 3: Catalyst reduction

Catalyst from Example 2 (20ml) was mixed with 70 ml of 1-2 mm quartz particles. The mixture was placed into a 25 mm ID quartz reactor. The mixture was held in place with a layer of about 10 ml of the 1-2 mm quartz particles at the bottom of the reactor. The catalyst/quartz mixture was placed into the reactor one layer at a time with the individual layers being about 0.5 to 0.7 cc thick, until the entire volume of catalyst plus quartz was in the reactor. Hydrogen was passed through the reactor at ambient temperature and pressure at a gas hourly space velocity (GHSV) of  $100 \text{ hr}^{-1}$  for 15 minutes. Prior to being admitted to the reactor, the hydrogen was passed through a column of potassium hydroxide pellets to ensure removal of impurities. The reactor temperature was increased to 400°C over about 45 minutes, held for five hours, and allowed to return to ambient, all under flowing hydrogen. The hydrogen flow was then

replaced with a 2:1 blend of hydrogen and carbon monoxide synthesis gas at 100 hr<sup>-1</sup> GHSV for 15 minutes at atmospheric pressure. The synthesis gas was also passed through KOH pellets prior to being admitted to the reactor. The valves were then closed to the reactor thereby storing the catalyst under the synthesis gas blend.

#### Example 4: Catalyst Testing

The flow of synthesis gas was resumed into a reactor as in Example 3 and the reactor temperature increased from ambient to 140°C over about 40 minutes and the held for five hours. The temperature was allowed to return to ambient under flowing synthesis gas and the catalyst stored as in Example 3. Testing was resumed the next day by repeating the procedure with the exception of raising the temperature 10°C. this procedure was repeated until the optimum operating temperature was determined. The optimum operating temperature was that where the yield of C5+ products was maximized by measuring the grams of C5+ products produced per standard cubic meter of synthesis gas blend fed into the reactor. A decline in the yield of C5+ products produced indicated that the previous temperature was the optimum operating temperature. Catalyst performance was determined by measuring the gas contraction, products gas composition by gas chromatography and C5+ liquid product yield. The C5+ products were recovered from the reactor effluent using two traps. The first trap was water cooled and the second cooled with dry ice/acetone (-80°C). The C5+ product in the first trap was weighed directly. The product in the second trap was warmed to room temperature to volatilize C4- components and then weighed. The combined weights from the two traps was the yield. The C5+ product from the optimum temperature was further analyzed to determine hydrocarbon type and carbon chain length distribution. At random intervals, the

C5+ products from the non-optimum temperature tests were combined and analyzed. The results are shown the Table.

In the Table, the Schultz-Flory Alpha determination is an indication of the tendency of the synthesis to produce the next higher hydrocarbon product. Higher numbers are desirable. Methane yield, therefore, is the opposite, i.e. since higher products are desirable, a lower methane yield and conversion are positive results. It will be seen by the Table that, among reducible metals recognized as promoters, only rhenium, ruthenium and palladium unexpectedly produce an increase in at least one of the desirable parameters measured in the test. Rhenium and ruthenium have lower optimum temperatures than the unpromoted catalyst, an indication of superior performance. The catalyst promoted with rhenium also demonstrates a higher C5+ selectivity and Schultz-Flory Alpha than the unpromoted catalyst. The Ruthenium promoted catalyst had the highest CO conversion at its optimum, indicating a high intrinsic activity. While the palladium promoted catalyst did not have a lower optimum temperature, it did demonstrate higher selectivity for C5+ products. By contrast, the results show that the platinum promoter catalyst was clearly unacceptable by all criteria utilized.

Table

Metal Promoter	Wt. %	Optimum Temp °C	CO Conversion %	Yield g/cu meter Syngas		Selectivity % of CO Converted		Schulz-Flory Alpha
				CH4	C5+	CH4	C5+	
None	--	180	88	11	139	6	84	0.85
Rhenium	0.5	160	67	7	127	4	94	0.86
Ruthenium	0.5	170	91	15	147	8	83	0.81
Palladium	0.5	180	74	11	127	6	88	0.83
Cobalt	10.0	170	70	10	137	6	88	0.87
Iron	3.0	170	56	7	99	5	92	0.85
Platinum	0.5	220	38	12	23	31	14	----

WHAT IS CLAIMED IS:

1. A process for the formation of an enhanced dispersed active metal (DAM) catalyst for conducting hydrogenation reactions comprising:
  - a) forming a slurry of particulate DAM catalyst characterized by the capacity to form more than one oxide in a suitable fluid;
  - b) contacting the particulate DAM catalyst in the slurry with an oxidizing agent at temperatures below 200°C for a time such that the metals no longer exhibit uncontrollable pyrophoricity, thereby forming an oxidized catalyst precursor comprising said metals and at least one of hydroxides thereof and oxides thereof, wherein at least a portion of said hydroxides and oxides are in the lower oxidation state of the metals;
  - c) adding to said oxidized catalyst precursor a solution in a suitable solvent of one or more reducible salts of promoter metals selected from the group of rhenium, ruthenium, palladium, iron and cobalt;
  - d) recovering and drying said oxidized catalyst precursor and said salt; and
  - e) forming an active catalyst by treating the oxidized catalyst precursor with hydrogen at elevated temperature, wherein said one or more salts will be reduced during the hydrogen treatment to form the metal.
2. A process in accordance with Claim 1, wherein the oxidized catalyst precursor is recovered and dried prior to being combined with said solution in step c).

3. A process in accordance with Claim 2, wherein said one or more salts is soluble in water and said solution in step c) is an aqueous solution.

4. A process in accordance with Claim 1, wherein the fluid forming the slurry comprises water and the oxidized catalyst precursor includes hydroxides of the dispersed active metals.

5. A process in accordance with Claim 4, wherein said one or more salts is soluble in water and steps b) and c) are carried out simultaneously.

6. A process in accordance with Claim 5, wherein said salts are nitrates.

7. A process in accordance with Claim 1, wherein step b) is carried out at a temperature below 100°C.

8. A process in accordance with Claim 1, wherein in step d) the mixture of said oxidized catalyst precursor and said one or more salts is dried in air at a temperature above 100°C for at least one hour.

9. A process in accordance with Claim 1, wherein in step d) the mixture of said oxidized catalyst precursor and said one or more salts is dried under an inert atmosphere.

10. A process in accordance with Claim 1, wherein said metal is rhenium and said salt is ammonium perrhenate.

11. A process in accordance with Claim 1, wherein said metal is ruthenium and said salt is ruthenium trichloride.

12. A process in accordance with Claim 1, wherein said metal is cobalt and said salt is cobalt nitrate.

13. A process in accordance with Claim 1, wherein step e) is heating said mixture in air to a temperature of about 400° for a time sufficient to form the promoter metal from said one or more reducible salts thereof.

14. An enhanced catalyst formed by the process of Claim 1.

15. An enhanced catalyst in accordance with Claim 14, wherein said promoter metal is rhenium.

16. An enhanced catalyst in accordance with Claim 14, wherein said promoter metal is ruthenium.

17. An enhanced catalyst in accordance with Claim 14, wherein said promoter metal is cobalt.

18. A process for producing higher hydrocarbons by the hydrogenation of carbon monoxide by reaction with hydrogen at reaction conditions in the presence of an enhanced catalyst according to Claim 14.

19. A process in accordance with Claim 18, wherein at least a portion of the hydrocarbons formed are upgraded to more valuable products by at least one of fractionation and conversion operations.



FISCHER-TROPSCH CATALYST ENHANCEMENT (JSS-0005)

Abstract of the Disclosure

A process of enhancing both the activity and the methane selectivity of a Dispersed Active Metal ("DAM") hydrogenation catalyst is disclosed wherein the DAM undergoes low temperature oxidation in a slurry phase to form a stable, unique oxidized catalyst precursor that is subsequently reduced to form an enhanced catalyst by treatment with hydrogen-containing gas at elevated temperature, wherein reducible promoter metals comprising one or more of rhenium, ruthenium, palladium, iron and cobalt are added to the DAM. The promoter metals are mixed with the oxidized catalyst precursor as a solution of their reducible salts. The oxidized catalyst precursors are again recovered from the mixture and treated with hydrogen-containing gas to simultaneously form the metals and reactivate the DAM catalyst.

**DECLARATION FOR PATENT APPLICATION**Case Docket No. JSS-0005

As below named inventor(s)

Alla Jurlevna Krylova  
Michel A. DaageAlbert L'vovich Lapidus  
Russell John Koveal

Lilia Vadimovna Sineva

We/I hereby declare that residence, post office address and citizenship are as stated on page 2.

We/I believe we/I are the original, first and joint inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled **FISCHER-TROPSCH CATALYST ENHANCEMENT**, the specification of which(check one) ☒ is attached hereto.☐ was filed on \_\_\_\_\_ as Application Serial No. \_\_\_\_\_  
and was amended on \_\_\_\_\_ (if applicable).

We/I hereby state that we/I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

We/I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

We/I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate(s) listed below and have also identified below any foreign application(s) for patent or inventor's certificate(s) having a filing date before that of the application on which priority is claimed:

**Prior Foreign Application(s)****Priority Claimed**

(Number)	(Country)	(Day/Month/Year Filed)
_____	_____	_____
(Number)	(Country)	(Day/Month/Year Filed)
_____	_____	_____

<input type="checkbox"/>	<input type="checkbox"/>
Yes	No
<input type="checkbox"/>	<input type="checkbox"/>
Yes	No

We/I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, we/I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
_____	_____	(patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status)
_____	_____	(patented, pending, abandoned)

We/I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)	(Filing Date)
_____	_____
(Application Serial No.)	(Filing Date)
_____	_____

POWER OF ATTORNEY: As named inventor(s), we/I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

**NAMES**  
 JAY SIMON  
 JONATHAN N. PROVOOST

**REGISTRATION NUMBERS**  
 23,067  
 44,292
**SEND CORRESPONDENCE TO:**
 EXXONMOBIL RESEARCH AND ENGINEERING COMPANY  
 (formerly Exxon Research and Engineering Company)  
 P. O. Box 390  
 Florham Park, New Jersey 07932-0390
**DIRECT TELEPHONE CALLS TO:**  
(Name and Telephone Number)
 JAY SIMON  
 (973) 765-1580

We/I hereby declare that all statements made herein of our/my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF INVENTOR	LAST NAME KRYLOVA	FIRST NAME ALLA	MIDDLE NAME JURIEVNA
RESIDENCE & CITIZENSHIP	CITY MOSCOW	STATE OR FOREIGN COUNTRY RUSSIA	COUNTRY OF CITIZENSHIP RUSSIA
POST OFFICE ADDRESS	POST OFFICE ADDRESS GRAIVOROVSKAYA, d.21, Kv.12	CITY MOSCOW	STATE OR COUNTRY RUSSIA
			ZIP CODE 109518

Inventor's Signature Alla Jurievna KrylovaDate 6/24/2000

FULL NAME OF INVENTOR	LAST NAME LAPIDUS	FIRST NAME ALBERT	MIDDLE NAME L'VOVICH
RESIDENCE & CITIZENSHIP	CITY MOSCOW	STATE OR FOREIGN COUNTRY RUSSIA	COUNTRY OF CITIZENSHIP RUSSIA
POST OFFICE ADDRESS	POST OFFICE ADDRESS KASHIRSKOYE SHOSSE, d.28, K.1V1.43	CITY MOSCOW	STATE OR COUNTRY RUSSIA
			ZIP CODE 115522

Inventor's Signature Albert Lvovich LapidusDate 6/27/2000

FULL NAME OF INVENTOR	LAST NAME SINEVA	FIRST NAME LILIA	MIDDLE NAME VADIMOVNA
RESIDENCE & CITIZENSHIP	CITY MOSCOW	STATE OR FOREIGN COUNTRY RUSSIA	COUNTRY OF CITIZENSHIP RUSSIA
POST OFFICE ADDRESS	POST OFFICE ADDRESS USSURIYSKAYA ST., 5-1-33	CITY MOSCOW	STATE OR COUNTRY RUSSIA
			ZIP CODE 107065

Inventor's Signature Lilia Vadimovna SinevaDate 6/24/2000

FULL NAME OF INVENTOR	LAST NAME DAAGE	FIRST NAME MICHEL	MIDDLE NAME A.
RESIDENCE & CITIZENSHIP	CITY BATON ROUGE	STATE OR FOREIGN COUNTRY LOUISIANA	COUNTRY OF CITIZENSHIP FRANCE
POST OFFICE ADDRESS	POST OFFICE ADDRESS 530 HIGHLAND TRACE DRIVE	CITY BATON ROUGE	STATE OR COUNTRY LOUISIANA
			ZIP CODE 70810

Inventor's Signature Michel A. DaageDate 6/6/00

FULL NAME OF INVENTOR	LAST NAME KOVEAL	FIRST NAME RUSSELL	MIDDLE NAME JOHN
RESIDENCE & CITIZENSHIP	CITY BATON ROUGE	STATE OR FOREIGN COUNTRY LOUISIANA	COUNTRY OF CITIZENSHIP USA
POST OFFICE ADDRESS	POST OFFICE ADDRESS 4732 BEECH HARBOR	CITY BATON ROUGE	STATE OR COUNTRY LOUISIANA
			ZIP CODE 70817

Inventor's Signature Russell John KovealDate 6/6/00

FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY
			ZIP CODE

Inventor's Signature \_\_\_\_\_

Date \_\_\_\_\_